

Using SEPS as A Novel Modifier for Bitumen

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Abstract

The unique properties (high flexibility, high traction, sealing abilities, heat resistant) of Kratons such as SEPS and their considerable effects on improving the original bitumen properties, encouraged using these additives as effective modifiers. In this study, soft base asphalt has been modified by addition of different amounts of SEPS and the rheological properties and hot storage stability of the Polymer Modified Bitumens (PMBs) have been studied, several tests have been conducted to determine the resulted effects, such as classical tests and rheological analysis. The results of classic tests showed that adding SEPS reduced penetration, temperature susceptibility, and ductility and increased the softening point and elastic recovery. Rheological properties of modified specimens were investigated with DSR in temperature sweep and frequency sweep and creep tests before and after aging in RTFO. The results indicated that the rheology of the modified binders is largely dependent on the polymer content. At low polymer content, the modified binders showed dispersed polymer particles in a continuous bitumen matrix. At a sufficiently high polymer contents, a continuous polymer phase was observed. Regardless of the nature of the two phases, the storage stability of the modified binders decreased as polymer content increased. Polymer modification improved bitumen rheological properties such as the increased elastic responses at high temperatures and the reduced creep stiffness. In this study the FTIR test was employed to investigate the chemical bonding changes of neat and polymer modified asphalt and the results proved the strong interaction between polymer and bitumen due to creation of new chemical bonds.

Keywords

SEPS; Polymer Modified Bitumen; Rheology; Aging; FTIR

Introduction

In the recent decades asphalts are widely employed in several applications, but the most important one is related to the paving industry. Unfortunately, high-temperature rutting and low temperature cracking of asphalt cement or coating layer due to severe temperature susceptibility limits its further application. Therefore, the improvements of functional properties

are necessary. The properties of PMBs are dependent on the polymer characteristics and content and bitumen nature, as well as the blending process.

Asphalt mixtures with a high stiffness modulus at low temperatures are most prone to low-temperature cracking. To reduce the risk of this type of cracking, the binder should have good flexibility (low stiffness and high ability of stress relaxation) at the lowest pavement temperature.

In this context styrene – (ethylene-co-propylene) – styrene triblock copolymers (SEPS) is used to modify bitumen. SEPS offers many of the properties of natural rubber, such as flexibility, high traction, and sealing abilities, but with increased resistance to heat, weathering, and chemicals and regardless of its wide applications for adhesive adhesives, sealants and coatings, it is not used in asphalt modification so far.

In this study, bitumen has been modified by addition of different amounts of SEPS and the rheological properties and hot storage stability of the PMBs have been studied. The master curves of the viscoelastic material functions have been prepared in linear conditions over a wide frequency range. The results, combined with viscosity measurements, the outcomes of classical tests, explain some structure property relationships and allow the determination of the range of compositions where stable mixes can be obtained. Fourier Transform Infrared Spectrums (FTIR) of all unaged and aged samples has been investigated. The detailed tests and discussions of the results obtained from the testing are discussed in the following sections.

Materials and Methods

Material and Sample Preparation

One bitumen from vacuum distillation of 85/100 Pen grade was blended with 2, 4 and 6 percentages of Styrene–ethylene–propylene–styrene block copolymer (SEPS). The SEPS polymer is Kraton G1780M (Shell),

containing 7 wt % styrene. The typical mixing procedure is as follows: aluminum cans of approximately 500 cc were filled with 250 – 260 g of asphalt and put in a thermoelectric heater. When the asphalt temperature reached 180 °C, a high shear mixer was dipped into the can and set to 4000 rpm. In the first stage, specific amount of SEPS were added to bitumen gradually (about 5 g/min) while keeping the temperature within the range of 180±1 °C during the polymer addition and the subsequent 2h of mixing. Finally, the obtained Polymer Modified Asphalt (PMB) was split in appropriate amounts to prepare samples for characterization. The samples were stored in a refrigerator at -20 °C.

1) Aging Procedures

All bitumen samples were aged by rolling thin film oven test (RTFOT) (ASTM D method 2872-85) in order to simulate the plant hot mixing process.

2) Storage Stability

The hot storage stability test consists of keeping the PMB in a test tube stored in a vertical position at 180 °C for 72±1 h and then taking samples from the top and bottom part was done. The difference of TR&B between the two samples indicates what proportion of the SEPS is separated and migrates to the lower or upper layers of the tube, due to its density difference in comparison with asphalt and the complex modulus of top and bottom parts shows how they are different in terms of rheological properties.

Classical Tests

All of the asphalt binder samples were analyzed through the following classical methods: Penetration (ASTM method D5), Ring and Ball Softening Point (ASTM method D36) and Elastic Recovery using a Ductilometer (ASTM method 6084-97) and Rotational Viscosity (ASTM method D4402). The elastic recovery test evaluates the ability of the binder to stretch and recover elastically.

Dynamic Rheological Characterization

Dynamic Shear Rheometer (DSR) MCR101 from Austria Anton Paar Company was used in this study for generating the dynamic data for the bitumen. The parameters for the DSR are in the following TABLES 1 and 2. The repeated shear creep test with a loading and recovery period was conducted on bitumen by DSR. The creep tests were done under 2 fixed shear

stresses of 100 and 3200 Pa with totally 100 (s) loading time and 100 (s) recovery time at 50°C.

TABLE 1 PARAMETERS FOR FREQUENCY SWEEP

Temperature(°C)	D ^a (mm)	H ^b (mm)	Fre ^c . (rad/s)
10,20	8	2	0.1-1000
30,40, 50 , 60	25	1	0.1-1000

^a Diameter of the plate

^b Gap between the plates

^c Sweep frequency

TABLE 2 PARAMETERS FOR TEMPERATURE SWEEP TEST

Temperature(°C)	30°C to 90°C
D(mm)	25
h(mm)	2
Fre.(rad/s)	10rad/s
Strain(%)	1%
Temperature rising rate	2°C/min

Results and Discussion

All of the asphalt binder samples in this study were submitted to the same heating treatment to avoid any difference in their properties caused by the high temperature used during their preparation.

Conventional Binder Tests

The effect of SEPS polymer modification on the conventional binder properties can be seen in TABLE 3. It can be observed that there is a decrease in penetration and an increase in the softening point with the polymer addition. As expected, the modified asphalt samples had a reduced penetration and higher softening point and elastic recovery indicating an improvement in the asphalt binder stiffness and flexibility. These modified samples are thus more adequate for paving applications, since they will be more resistant to rutting, fatigue and plastic deformation.

TABLE 3 CONVENTIONAL PROPERTIES OF SEPS PMB

Sample	Softeningpoint °C	Penetration (mm)	Ductility (cm)	Elastic recovery(%)
neat bitumen	43.3	108	160	-
bitumen+2% SEPS	46.5	76	52	15
bitumen+4% SEPS	78.3	56	47.6	100
bitumen+6% SEPS	87.9	45	47	100

However, the conventional tests results strongly depend on polymer content. The Elastic recovery, softening point for samples containing 4 and 6% SEPS dramatically increased in comparison with neat bitumen and binder with 2% SEPS. This may be the result of creation of polymer continuous phase.

The values for the Rotational viscosity of the SEPS PMB samples as a function of the SEPS content FIG. 1.

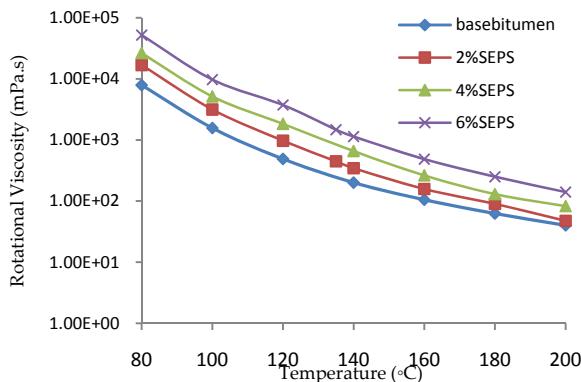


FIG.1 ROTATIONAL VISCOSITY VS. TEMPERATURE

As expected, there is an increase in the asphalt viscosity with the polymer addition. The Brookfield viscosity variation is in agreement with the softening point values of the SEPS PMB. A PMB with high viscosity favors a thicker film formation surrounding the aggregates which increases the cohesive forces between the components and gives the expected improvement in the paving in terms of resistance to water and environmental conditions at operating temperatures. On the other hand, by increasing the temperature the difference in viscosity between the PMB samples decreases, which favors the polymer mixing during the asphalt modification and paving application.

Storage Stability

As described previously, a tube test was used to determine the storage stability of polymer modified bitumens. After vertically storing the tube at 180 °C for three days, DSR (temperature sweeps between 30 and 90 °C) at 10 rad/s and also softening points(TABLE 4) of the samples taken from the top and bottom of the tubes has been investigated and compared with binders before hot storage.

TABLE 4 STORAGE STABILITY OF BINDERS

Samples	Temperature°C		
	Top	Bottom	T _{top} -T _{bottom}
Neat bitumen	44.3	44.3	0
Bitumen+2% SEPS	47.4	47.6	0.2
Bitumen+4% SEPS	77.4	76.9	0.5
Bitumen+6% SEPS	82.7	73.9	8.8

Moreover, the logarithm of the ratio of G* of the bottom of the tubes to G* of top of the tubes is defined

as the separation index, I s. DSR results obtained at 10 rad/s are plotted in FIG. 2.

The acceptable stability of the specimen is if the difference between the softening point of top and bottom of the sample is below 2.5 °C. The difference between the softening points indicates how stable the mixture is. As TABLE 4 shows the differences between the top and bottom softening points in all samples, except sample with 6% SEPS, are less than 2.5 °C. The less difference between complex modulus of top and bottom there is, the more stable binders are .As FIG. 2 shows samples containing 2 and 4% SEPS have zero separation index. At low polymer concentrations, the content of maltenes (more compatible with the polymer) is probably sufficient to swell the macromolecules without inducing instability in the micellar structure of asphalt, and the resins may stabilize the polymer-rich phase as they are supposed to do with asphaltenes, with the result that no phase separation occurs. At higher polymer concentrations, a larger quantity of polar aromatics is subtracted from maltenes and, therefore, the colloidal structure of asphaltene micelles or micellar aggregates is no longer stabilized and tends to collapse.

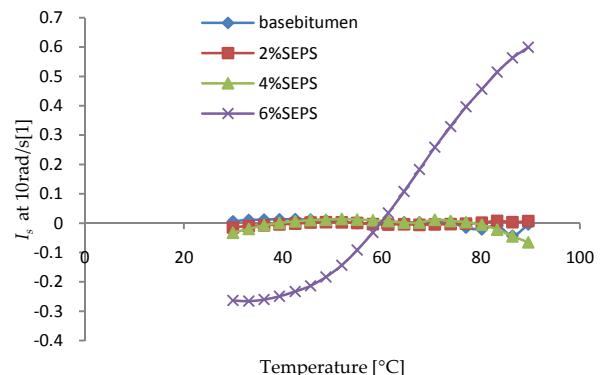


FIG. 2 THE ISOCHRONAL PLOT OF SEPARATION INDEX (I_s) FOR BINDERS AT 10 RAD/S.

Rheological Properties

The rheological characterization allowed building master curves from the dynamic data taken in isothermal frequency sweep tests. The time-temperature superposition principle was found to hold for all the investigated materials and the horizontal shifting factor was satisfactorily described by the WLF relation. In DSR, G* is a measure of the overall resistance to deformation of a material. FIG. 3 plotted the G* of binders over a wide range of frequencies for RTFO aged samples.

At high frequencies (low temperatures) no significant differences are detectable between the four binders. This is not surprising because it is well known that similar systems have almost universal behavior when the glass transition region is approached. At lower frequencies, the difference between binders with 4 and 6% Polymer and 0 and 2% Polymer is significant. With a small polymer quantity, the PMB is similar to neat bitumen and polymer acts as filler rather than a real modifier and has an effect mainly on the moduli values. However, in samples with more polymer content the binders are more likely to have a polymeric behavior.

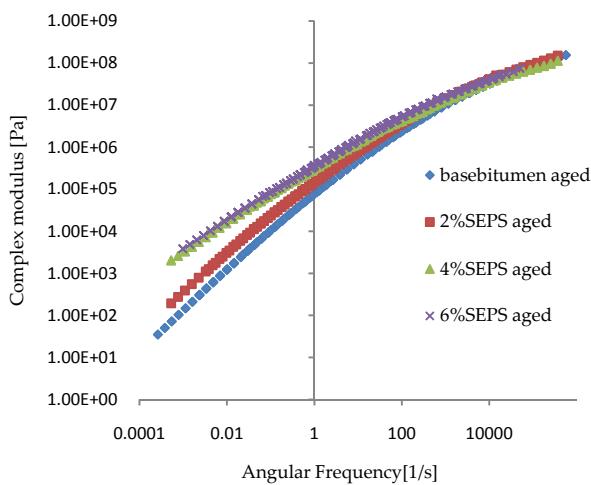


FIG. 3 THE MASTER CURVE OF RTFO AGED SAMPLES AT 30 °C

As mentioned before, for bitumens and PMBs, complex modulus G^* is a measure of the overall resistance to deformation, while phase angle reflects the viscoelastic character. These binder parameters are critical for asphalt performance in the field, e.g. resistance to rutting and cracking. Examples of complex modulus versus phase angle obtained by frequency sweep at 30°C for unaged and RTFO aged are shown in FIG. 4. In bitumen area, this type of plot is called Black Diagram, by which the rheological changes as related to pavement performance, e.g. resistance to permanent deformation, can be easily characterized when modified and unmodified bitumens are compared. The curve of 2% SEPS appears almost superposed over that of base bitumen. The differences among the curves become more and more evident in shape and absolute values when a greater quantities of polymer (4 and 6%) are added and the curves show a sort of plateau in G^* which strongly highlights how the polymer affects the properties of the binder. Moreover, it is remarkable that for 4 and 6 % polymer the samples became more elastic by decreasing and increasing the complex

modulus and frequency. The difference between the curves decreased after RTFO aging and all the samples shifted to lower phase angles that are the causes of hardening.

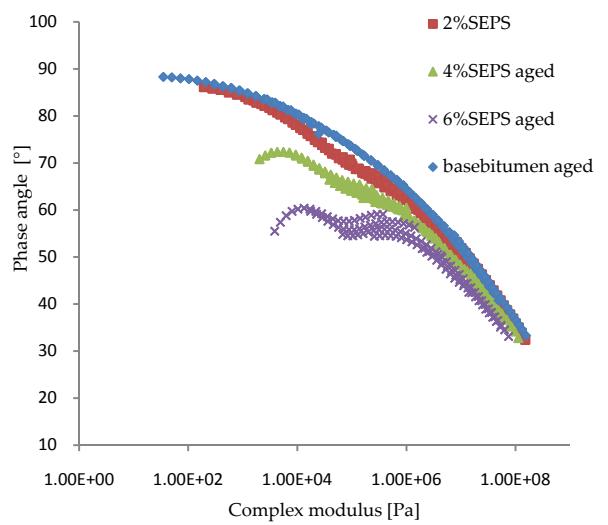


FIG. 4 THE BLACK DIAGRAM OF RTFO AGED SAMPLES AT 30 °C

The most significant effect of polymers on asphalt is the improvement of elasticity. There is a strong correlation between rutting resistance at high temperature and complex modulus. Increasing complex modulus (elastic modulus) is to be expected because it reflects a promising rutting resistance at high temperature.

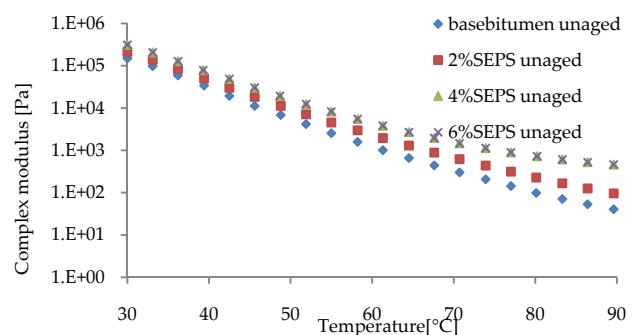


FIG. 5(A) COMPLEX MODULUS OF UNAGED SAMPLES

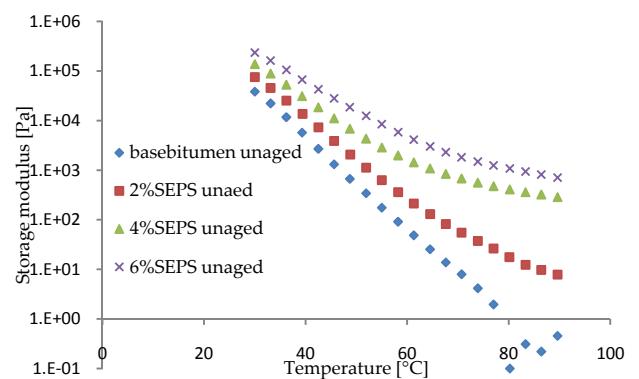


FIG. 5(B) STORAGE MODULUS OF UNAGED SAMPLES

Isochronal plots of complex modulus (G^*), Storage modulus(G') and damping factor $\tan\delta$, versus temperature at 10 rad/s for SEPS modified asphalts (before aging) are shown in FIG. 5(a), (b), (c) respectively.

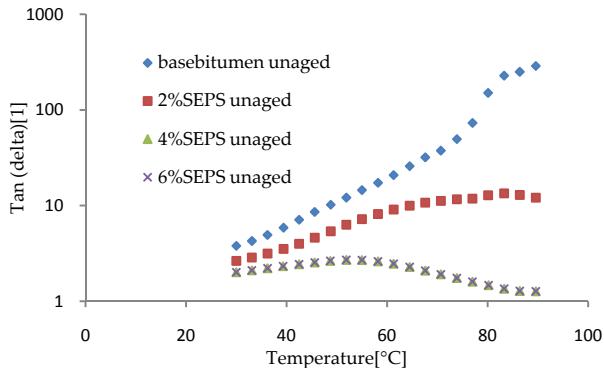


FIG.5 (C) DAMPING FACTOR OF UNAGED SAMPLES

The isochronal plots show a difference between the base asphalt and the SEPS modified asphalt, particularly at lower end of the temperature range. With increasing SEPS content, there is a significant increase in G^* and G' and over entire temperature range especially for 4% or 6% SEPS modified asphalt, which is an evidence of dominant polymer network. Furthermore, the polymer addition to the asphalt caused a considerable reduction in the $\tan\delta$ values and this result signifies an improvement in the PMB elastic response. $\tan\delta$ is related to the G''/G' ratio and a decrease in this ratio indicates that the PMB has a higher storage modulus or improved elastic property. Thus, the formation of a polymer network in the asphalt binder leads to a lower plastic deformation. There is considerable evidence of extreme polymeric modification(for 4% and 6% SEPS) at high temperatures with the establishment of a plateau region in the $\tan\delta$ curve of the all PMB samples, which is indicative of the formation of a dominant polymer network in the asphalt matrix with decreased viscosity. On the other hand, the plateau regions and decreased $\tan\delta$ at intermediate and high temperatures are synonymies with the plateau region defined for polymers and demonstrates the ability of the polymer to form a continuous elastic network especially for SEPS (high content) modified asphalt.

Oxidative ageing causes hardening of bitumen and degradation of polymer, and consequently, changes in the rheological properties of polymer modified binders. Oxidative ageing causes hardening of bitumen and degradation of polymer, and consequently, changes in the rheological properties of polymer

modified binders. These changes are mainly due to the oxidative hardening of the bitumen. FIG. 6(a), (b), (c) plotted complex modulus (G^*), Storage modulus (G') and damping factor $\tan\delta$ vs. temperature respectively for RTFO aged samples.

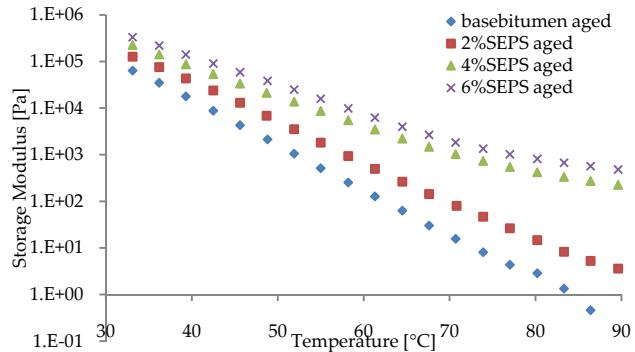


FIG. 6(A) STORAGE MODULUS FOR RTFO AGED SAMPLES

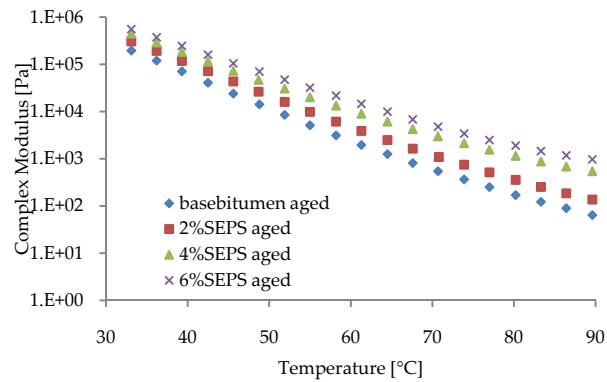


FIG. 6(B) COMPLEX MODULUS FOR RTFO AGED SAMPLES

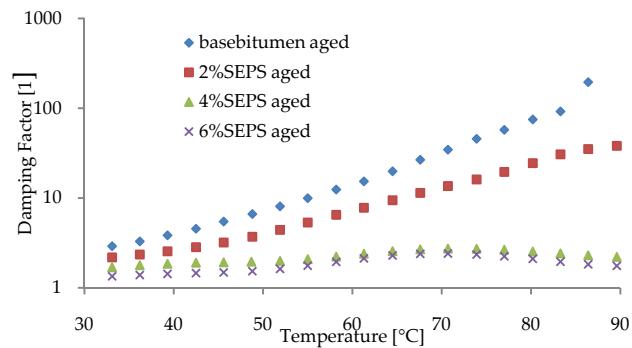


FIG. 6(c) DAMPING FACTOR FOR RTFO AGED SAMPLES

Effect of temperature on $G^*/\sin\delta$ is shown in FIG. 7 for both aged and unaged samples. The Super-pave parameter $G^*/\sin\delta$ was specified as the stiffness indicator for evaluating the rutting resistance of both unmodified and polymer modified binders. Rutting is defined as the progressive accumulation of permanent deformation of each layer of the pavement structure under repetitive loading. Obtained results indicate that for unaged and aged specimens this parameter considerably increased by increasing the SEPS content.

Thus, SEPS addition to the asphalt enhances the $G^*/\sin\delta$ value and triggered in high resistance to permanent deformation and this extends the temperature range within which it can be used.

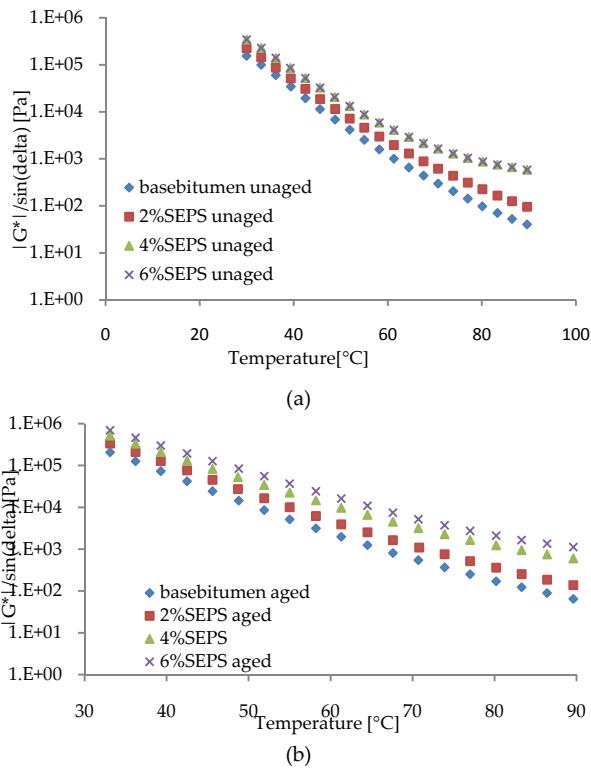


FIG. 7 RUTTING FACTOR FOR UNAGED(A) AND RTFO AGED (B) SAMPLES

The results of creep test at 50 °C have been shown in FIG. 8. At each loading cycle, the loading and recovery time was equal to 1s and 9s, respectively and loading cycles repeated for 20 times (10 cycles with 100 Pa loading and 10 cycles with 3200Pa loading). Instantaneous elastic strain of asphalt developed during the stage of loading stress, and the viscoelastic strain of asphalt accumulated to the total creep strain at the time of unloading. The instantaneous elastic strain of asphalt disappeared after unloading, and the delayed elastic stain recovered gradually. The unrecoverable viscoelastic strain is the permanent strain.

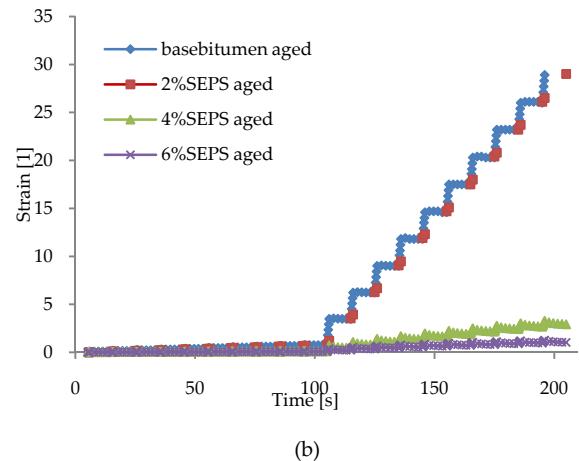
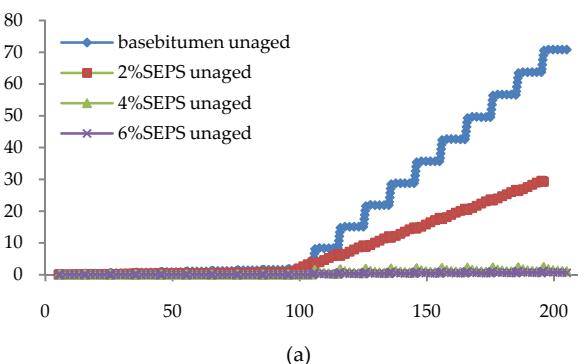


FIG. 8 THE RESULTS OF CREEP TEST OF BITUMEN BINDERS AT 50 OC FOR (A)UNAGED AND (B) AGED SAMPLES

Results indicate that increasing the SEPS content and aging in RTFO have noticeable effect on reducing the creep. The residual strain for samples containing 4% and 6% SEPS is extremely close to zero and this fact is a strong evidence of creation of polymeric network and continuous phase. As shown in these Figures, for all cases the differences between obtained diagrams have increased by increasing the number of cycles. After RTFO aging the creep resilience decreased for PMBs and this can be result of polymer degradation.

FTIR Spectroscopy

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. In this study the FTIR test was employed to investigate the chemical bonding changes of neat and polymer modified asphalt and the results are shown in FIG. 9. In the Figure, the strong peaks around 2850 cm^{-1} and 2920 cm^{-1} are typical C-H stretching vibrations in aliphatic chains. The band at around 1030 cm^{-1} is assigned to stretching sulfoxide. The aliphatic branched band (bending C-H of CH 3) and aliphatic index band (bending C-H of - (CH 2)n-) are observed at 1376 cm^{-1} and 1460 cm^{-1} respectively. The 1600 cm^{-1} and 1690 cm^{-1} bands correspond to the aromatic band (stretching C=C aromatic) and carbonyl band, (stretching C=O conjugated). As it can be seen by adding the SEPS content the peaks area around 690 to 800 cm^{-1} (related to aromatic C-H) have increased. Whereas, the areas for stretching OH group, centering around 3742 cm^{-1} has increased by adding SEPS which proves the creation of chemical interactions between polymer and asphalt.

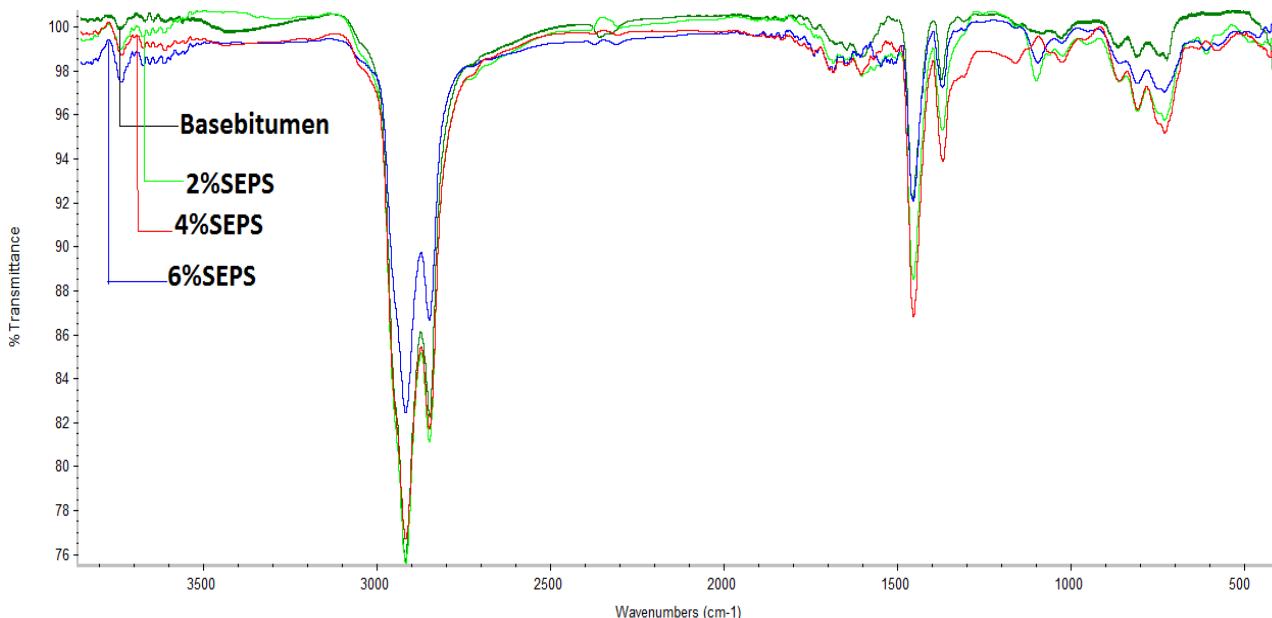


FIG. 9 THE FTIR OF BITUMEN BINDERS

Conclusion

In comparison with the neat bitumen, SEPS modified binders demonstrate more resistance to aging and better properties after RTFO aging, from FTIR results the creation of new chemical bonds between polymer and bitumen was proved.

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